Surface-induced layer formation in polyelectrolytes

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We analyze, by means of an RPA calculation, the conditions under which a mixture of oppositely charged polyelectrolytes can micro-segregate in the neighborhood of a charged surface creating a layered structure. A number of stable layers can be formed if the surface is sufficiently strongly charged even at temperatures at which the bulk of the mixture is homogeneous.

I. INTRODUCTION

It has been described in an article by Decher [1,2] a procedure for creating a coating for a (charged) surface that consist of alternating layers of two different, oppositely charged, polyelectrolyte homopolymers. The properties and uses of these systems has been explored by several groups [3–5]. The basic technology for the creation of these coatings is easy to describe. The starting surface is charged (say, positively) and it is first dipped into a solution of negatively charged homopolymers and then withdrawn from it. This forms a first layer since the polyelectrolyte is strongly attracted to the surface. The surface is washed and one gets rid of excess polymer chains that are only loosely tied to the surface. The surface is now dipped in a solution of the second homopolymer that is positively charged. This second homopolymer is strongly attracted to the coated surface, which is now effectively negatively charged. The process is repeated several times, and the layering is found to be stable. A more detailed exposition is presented in the original articles [1,2]. Figure 1 shows a schematic version of the layered system.
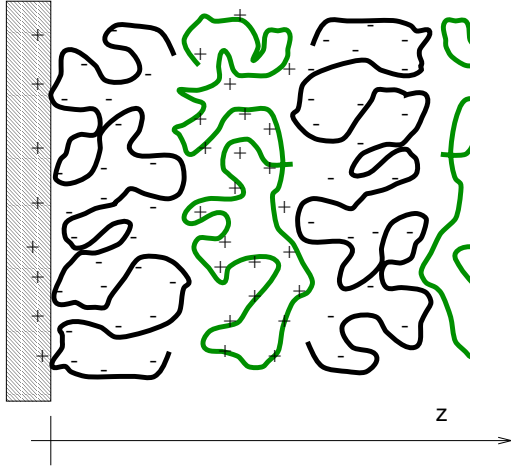

FIG. 1. Scheme of the layered structure formed by a mixture of polyelectrolytes near a flat surface. The surface is charged positively, attracting a negatively charged polymer. The second layer consist of polymers positively charged, attracted to the first charged layer, and so forth. Counterions are not shown in the scheme.

It has been argued from the theoretical point of view, [6–9] that lamellar and other microphase structures can occur in mixtures of oppositely charged polyelectrolytes. Usually, such phases are associated with block copolymers where chemical bonding is an impediment to macrophase separation. In charged polymer mixtures, the entropy of mixing of the counterions for each of the homopolymer species provides a huge barrier to macrophase formation, allowing instead for the possibility of microphases. In both cases, copolymers and polyelectrolytes, the separation is driven by the chemical repulsion between the species.

An interesting aspect of the above outlined procedure for manufacturing the lamellar structure is that it would seem to work even at temperatures or for ranges of parameters at which, in principle, a phase separation should not be observed. In the following we will analyze the conditions under which we can expect to find such stable morphologies. Above the transition point, an RPA approach will show that a finite number of these layers should be stable near the surface.

If the charged surface is immersed in a mixture of homopolymers, it will drive the spontaneous creation of a few number of layers that will then coexist with the bulk of the mixture. This case is slightly different to the one resulting from the dip-and-wash mechanical layering procedure in which the surface is only in contact with solutions of homopolymers. Both systems, however, should have similar stability conditions, the same relevant parameters, and generate comparable length scales for the layers. We will carry out our calculation for the case of the surface immersed in the polymer mixture, and consider the charged surface as a a large flat plate.

II. RPA FOR POLYELECTROLYTE MIXTURES

The fundamental fields for the description of the model system are the volume fraction of the homopolymers Φ_A and Φ_B. Both homopolymers will be considered to have the same monomer number N. A fraction f of the monomers in each chain carry charges z_A and z_B respectively and we will again consider only the most symmetric case $z = z_A = -z_B$. We consider the polymers to

be dense with a negligible amount of solvent, and consider the effective volume fraction occupied by the relative counterions very small. The local counterions densities are n_A and n_B. Counterions for polymers A and B carry charges $-z_A$, and $-z_B$.

The RPA approximation for a mixture of polyelectrolytes has been developed and studied by a number of groups [6–9]. With a number of further simplifications (to be described later), a particularly useful form of the RPA free energy functional has been written by Nyrkova *et al.* [9]. To their basic free energy, we add a term coupling the charge density to an external potential (that will be generated by the charged surface).

$$F = \int d\mathbf{r} \left\{ \frac{1}{N} \Phi_A \ln \Phi_A + \frac{1}{N} \Phi_B \ln \Phi_B + \chi \Phi_A \Phi B \right.$$
$$+ \frac{b}{36\Phi_A} (\nabla \Phi_A)^2 + \frac{b}{36\Phi_B} (\nabla \Phi_B)^2$$
$$\left. + n_A \ln n_A + n_B \ln n_B \right\}$$
$$+ \frac{Bj}{2} \int d\mathbf{r} \, d\mathbf{r}' \, \rho(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}') + \int d\mathbf{r} \, eV(\mathbf{r})\rho(\mathbf{r}) \quad (1)$$

In this expression, all energies are measured in units of $k_B T$, and the Kuhn length is b. The Bjerrum length is $Bj = e^2/(\epsilon k_B T)$. The interaction parameter χ is in this case positive, implying repulsion between species. The parameter χ is considered close to, but smaller than, the critical value required for the spontaneous creation of lamellar (or another) microstructure. The prefactor for the gradient terms is such that if we turn off the electrostatic interactions, the correlation functions will match the first terms of the Debye function for each type of chain, namely, in Fourier space $\langle \Phi_{\mathbf{k}} \Phi_{-\mathbf{k}} \rangle = C(1 + \frac{R^2}{3} k^2 + \ldots)$, with the radius of gyration $R^2 = b^2 N/6$. Lastly, the density of charged particles ρ is defined by

$$\rho = z_A(f_A \Phi_A - n_A) + z_B(f_B \Phi_B - z_B). \quad (2)$$

Thus, we have essentially a regular solution model in which Nyrkova *et al.* [9] argue that there are no important corrections arising from fluctuations. Further, the intra-chain correlations are reduced to pure random walks, and only the first derivatives of the fields appear in the functional. In reference [6] the full Debye function has been used to represent the intra-chain correlations, but the effect on the results here presented is minor, as the corrections appear at wavelengths smaller than the resulting layer thickness.

Since we are interested in the behavior of the mixture above the demixing temperature, we assume a base state with homogeneous distributions of homopolymers and counter-ions. The overall concentrations of polymers $\bar{\Phi}_A = \Phi_0$, $\bar{\Phi}_B = 1 - \Phi_0$ are considered as given, and the bulk concentrations of counter-ions are $\bar{n}_i = f\bar{\Phi}_i$, for each species. These overall concentrations should remain constant and the only important collective variables are the difference in the local concentrations between the species:

$$\Psi = \Phi_A - \Phi_B - (2\Phi_0 - 1) \quad (3)$$
$$n = n_A - n_B - f(2\Phi_0 - 1). \quad (4)$$

Since the volume fraction of the counterions is small compared to the volume fraction of the polymers, we set

$$\Phi_A + \Phi_B = 1, \quad (5)$$

to be satisfied everywhere.

The effective RPA free energy in terms of the Ψ, n variables is obtained by expanding all terms up to second order in the fields, and the result is

$$F = F_0 + \frac{Bj}{2} \int d\mathbf{r} \, d\mathbf{r}' \, \frac{(f\Psi(\mathbf{r}) - n(\mathbf{r}))(f\Psi(\mathbf{r}') - n(\mathbf{r}'))}{|\mathbf{r} - \mathbf{r}'|}$$
$$+ \int d\mathbf{r} \frac{1}{8\Phi_0(1 - \Phi_0)N} \left(\Psi^2 + \frac{b^2 N}{18} (\nabla \Psi)^2 + \frac{N}{f} n^2 \right)$$
$$- \int d\mathbf{r} \frac{\chi}{4} \Psi^2 + \int d\mathbf{r} \, V(\mathbf{r})ez(f\Psi(\mathbf{r}) - n(\mathbf{r})). \quad (6)$$

For our purposes, we need to Fourier transform all quantities ($\hat{\Psi}(\mathbf{k}) = \int d\mathbf{r} \, e^{-i\mathbf{k}\cdot\mathbf{r}} \Psi(\mathbf{r})$, and so forth) and rewrite the free energy as:

$$F = F_0 + \frac{Bj}{2} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{4\pi(f\hat{\Psi} - \hat{n})^2}{k^2} +$$
$$\int \frac{d\mathbf{k}}{(2\pi)^3} \frac{1}{8\Phi_0(1 - \Phi_0)N} \left(\hat{\Psi}^2 + \frac{k^2 N}{18} \hat{\Psi}^2 + \frac{N}{f} \hat{n}^2 \right)$$
$$- \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\chi}{4} \hat{\Psi}^2 + \int d\mathbf{k} \, ez\hat{V}(f\hat{\Psi} - \hat{n}). \quad (7)$$

III. RESPONSE TO EXTERNAL POTENTIALS AND SURFACE EFFECTS

For a given external potential $V(\mathbf{r})$, we can now calculate the general response of the system. We shall work out the response when the external potential originates from a pair of parallel charged surfaces, and then, in more detail, the case of only one bounding surface.

A. General effect of an external potential

Minimization of the free energy, eq.7, with respect to the polymer and counterion densities, gives a pair of coupled equations for $\hat{\Psi}$ and $\hat{n}$. To present the solutions in a more transparent manner, we will introduce a number of simplified and dimensionless variables, namely:

$$x = \frac{1}{2}r_0^2 k^2 = \frac{l^2 k^2}{18f}, \tag{8}$$

$$s = \frac{1}{fN}\left[1 - 2\chi N\Phi(1-\Phi)\right], \tag{9}$$

$$t = \frac{4\pi\Phi(1-\Phi)}{9}\frac{Bj}{b}. \tag{10}$$

$$\tag{11}$$

The variables s and t measure the strength of the interspecies and electrostatic interactions, while the variable x compares the wave-vectors against the the screening length of the counter-ions $r_0 = b(18f)^{-1/2}$.

Now the solution to the system reads

$$\hat{\Psi}(\mathbf{k}) = R_1(\mathbf{k})\hat{V}(\mathbf{k}) = \frac{[2x\Phi_0(1-\Phi_0)](-eV(\hat{\mathbf{k}}))}{D(\mathbf{k})} \tag{12}$$

$$\hat{n}(\mathbf{k}) = R_2(\mathbf{k})\hat{V}(\mathbf{k}) = \frac{[4f\Phi_0(1-\Phi_0)x(x+s)]\,eV(\hat{\mathbf{k}})}{D(\mathbf{k})} \tag{13}$$

where the denominator is

$$D(\mathbf{k}) = x^2 + (t+s)x + t(1+s), \tag{14}$$

and we have introduced a shorthand notation for the overall responses R_1, and R_2.

B. Response of a mixture bounded by two surfaces

We consider now a bulk of the mixture contained between two parallel surfaces. One of the surfaces is charged positively, with a surface charge density σ. The more realistic condition for the second surface is to take it as uncharged. In fact, this second surface can be an imaginary surface coinciding with the free surface of the mixture (in contact with, say, air). The amount of charge in the second surface determines the electrostatic potential difference between the two surfaces, which is the relevant driving force of the micro-segregation when we neglect non-linear terms. Thus, for simplicity, we consider instead the equivalent case in which one has two oppositely charged surfaces with equal absolute value of charge density $\sigma/2$, separated by a distance L. In the following, we take the z axis to be normal to the surface, and set the origin in the left surface.

From elementary electromagnetism, the potential created by the charged surfaces is, for values of the z coordinate between 0 and L

$$V(\mathbf{r}) = V(z) = \sigma L(\frac{L}{2} - z). \tag{15}$$

To use our Fourier transformed quantities, we extend the potential to the full z axis, by reflection at all planes with $z = nL$, with n an integer. This allows us to obtain a suitable boundary behavior for the field Ψ, and reduces the problem to consider a Fourier Series for the potential in the region $(-L, L)$ (using the reflection condition). The expansion for the potential is $V = \sum V_m e^{im\pi z/L}$, with coefficients

$$V_m = \begin{cases} \frac{2\sigma L}{\pi^2 m^2} & \text{m odd} \\ 0 & \text{m even.} \end{cases} \tag{16}$$

for The linear response to this potential is also expressed as a Fourier Series, and the coefficients for the the composition Ψ and the counterion density n are obtained immediately from the solution in eq. 13 by evaluation at the wavenumbers $\mathbf{k}_m$, $(k_x = m\pi/L, k_y = 0, k_z = 0)$:

$$\Psi_m = R_1(\mathbf{k}_m)V_m, \tag{17}$$

$$\hat{n}_m = R_2(\mathbf{k}_m)V_m. \tag{18}$$

C. Response to the presence of one surface.

The case of only one surface bounding the mixture is equivalent to the case considered in the previous subsection when we let the separation between the surfaces grow and effectively become infinite. The proper limit to consider for the Fourier transform of the potential is

$$\hat{V}(\mathbf{k}) = 2\sigma(2\pi)^2 \delta(k_x)\delta(k_y)\frac{1}{k_z^2}. \tag{19}$$

It is convenient to introduce a new parameter proportional to the charge density,

$$\gamma = 4e\sigma r_o^2 \Phi(1-\Phi), \tag{20}$$

which amounts to measure the surface charge density as the number of charges in a square area of side r_o.

In the final result, all quantities depend only on the z coordinate, and all relevant reference to the wave-vectors is only through $x = k_z^2/18f$. We obtain that the transform of the response in this limit can be expressed as

$$\hat{\Psi}(\mathbf{k}) = (2\pi)^2\delta(k_x)\delta(k_y)\frac{-\gamma}{x^2 + (s+t)x + t(1+s)}, \tag{21}$$

$$\hat{n}(\mathbf{k}) = (2\pi)^2\delta(k_x)\delta(k_y)\frac{f(x+s)\gamma}{x^2 + (s+t)x + t(1+s)}. \tag{22}$$

The denominator in these expressions is a real, even, quartic polynomial in $|\mathbf{k}|$, and real quadratic in terms of x.

In this mean field approximation, there is a transition to a micro-segregated phase when the roots of the polynomial become real. This occurs when, for a given value of t, the s variable becomes negative enough, namely, at

$$s_r = -2t^{1/2} + t, \tag{23}$$

and at that point, there are two pairs of double roots for the polynomial at

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$$x_r = \pm(t^{1/2} - t). \qquad (24)$$

We are interested in the region above (temperature-wise), but close to the transition point. In such a region, the susceptibility to the influence of the surface is high, and yet, when the surface disappears there will not be spontaneous micro-segregation. We can measure the distance from the transition point by the variable

$$\epsilon = (s_r - s)^{1/2}. \qquad (25)$$

In terms of this parameterization the response has a rather simple expression. In real space we find that the field Ψ consist of decaying oscillations away from the $z = 0$ plane, (*i.e.* the physical charged surface):

$$\Psi(z) = -\frac{\gamma}{\epsilon x_r^2} \exp\left(-\frac{\epsilon}{r_0} z\right) \cos\left(\frac{x_r^{1/2} z}{r_0}\right). \qquad (26)$$

IV. LAYERING

In the equilibrium compositional profile that we have obtained, eq. 26, a layer is represented by a peak (positive or negative) in the concentration variable. For a layer to be recognizable as such, the peak in the Ψ field has to be comparable in magnitude to 1 (in the case of symmetric mixtures) so that one of the components saturate a region in space thus forming a recognizable layer. Since the solution we have decays away from the surface, the number of layers that are formed is finite. It is clear that it is of interest to maximize the number of layers that are stable near the surface. We shall consider three ways, suggested by our results, in which this effect can be achieved.

First, we note that that the field amplitude decays over a characteristic length $\Gamma = r_0/\epsilon$. If we tune the charge at the surface so that the strength of the electric field is just enough to saturate the composition at the surface so that $\Psi = 1$ there, then layers will exist only up to a distance Γ away from the surface. The thickness of the layers is given by the wavelength of the oscillations $\lambda = r_0/2\pi x_r^{1/2}$, and therefore the number of layers formed near the surface is

$$\frac{\Gamma}{\lambda} = \frac{2\pi x_r^{1/2}}{\epsilon}. \qquad (27)$$

To acquire the largest number possible of layers in this way, we would like to make ϵ as small as possible. Thus one has to be as close as possible to the transition point for the number of layers to suitably increase. An important issue arises here, in that while the layering system has been observed, the actual transition has not been observed, with the most simple explanation available being that the parameter region at which the system will undergo a transition is out of the reach of physically realizable systems, but then, even the near-transition region (ϵ small), is as well hard to reach.

A second idea for the creation of a good number of layers is over-saturation. Since we are interested in attaining the $\Psi = 1$ condition repeatedly, consider the case in which the source strength (the surface charge) is so big that, mathematically, Ψ will have to achieve values well beyond 1. To make sense of this solution, let us neglect non-linear effects and simply assume that when the mathematical solution dictates a value for Ψ larger than 1 the physical system simply saturates and takes the value of 1 in that region. Then, even if we go to distances well beyond Γ, the condition $\Psi = 1$ will be satisfied many times away from the surface. To obtain m layers we need an amplitude $e^{m\lambda/\Gamma}$, so that

$$m \sim \log(\gamma/\gamma_0), \qquad (28)$$

where γ_0 is the effective surface charge density required to obtain saturation of one component at the surface, i.e. $\Psi = 1$. Schematically, we have the case shown in Figure 2. While this is obviously a rather crude approximation, we should point out that, at the linear response level, the thickness of the layers does not depend on the strength of the surface charge density and we can expect that the layers formed might still have roughly such a characteristic size. A proper theoretical treatment of the problem should take into account the effects of strong segregation caused by the surface.
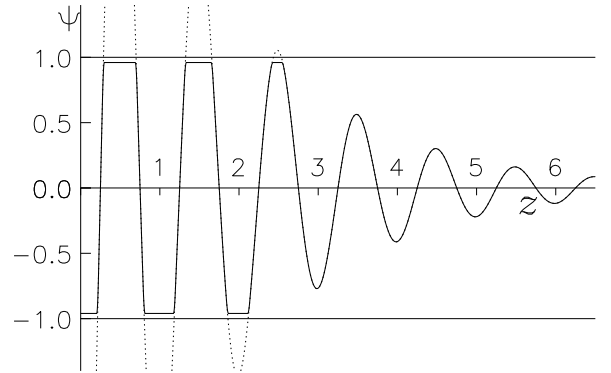

FIG. 2. The polymer composition profile Ψ, away from a charged surface. When the surface charge is large enough, the amplitude as obtained in eq.26 exceeds 1. Constructing profile for the composition by a simple truncation of this solution at the limiting values ± 1, we obtain important compositional fluctuations, even relatively far away from the surface.

It is also important to note that with this kind of argument we could attempt to reconcile the experimental observation of the layering process, with the fact that at the same time there is not know trace of the non-forced

microphase separation. This is, even when one operates far away from the critical point, a sufficiently large driving force can show the traces of the micro-segregation. For simplicity, we have presented our results in a form valid only in the neighborhood of the transition. For values of the parameters moderately distant from the transition point case, one should use the full response, and look at the complex roots of the denominator D to extract the wavelength, amplitude and decay length of the oscillations.

Finally, we return to finite size effects. A third idea to enhance the number of stable layers is to place the system in a finite geometry, as was described in section III. This is roughly equivalent to the experimental situation in which the layered system is taken away from the bulk of the mixture and has an overall finite thickness.

In the exploration of the limit when only one surface is present we have noticed that the oscillations of the homopolymers concentration decay relatively quickly. This needs not to be the case when we have a finite distance between the surfaces. First, if the distance between them is roughly about twice the decay length $L \sim 2\Gamma$, we will have, in the non over-saturated case, twice the number of layers expected from our estimate eq. 28, because of the association of the layers with each of the two surfaces. Further, the (possibly) constructive interference of the oscillations will make the amplitudes larger around the mid-point between the surfaces, creating a stronger segregation pattern. Secondly, we can try to match a multiple of the preferred wavelength $m\lambda$ with the distance between surfaces. Clearly, this resonance maximizes the segregation of the species. In Figure 3 we show the response constructed from our result eq. 17, for a distance between surfaces equal to 5.5 times the wavelength λ (9 layers).
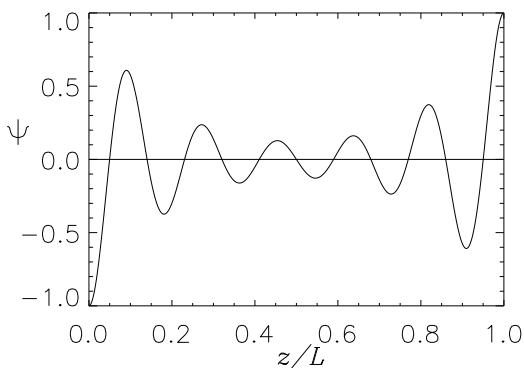

FIG. 3.   The polymer compositions profile Ψ for a finite slab of polymer mixture of width $L = 11\pi r_0/x_r^{1/2} = 38 r_0$. The values of the other basic parameters are $t = 0.5$, $s = -.91$.

V. DISCUSSION

Our description of the response to the charged surface has been presented in terms of a set of reduced variables, r_0, s, t. But it is necessary to comment on the values these quantities can achieve in actual systems. The simplest quantity is t. This is just a multiple of the Bjerrum length and we have it will always oscillate around a value of 1, taking values of, in some cases, $1/2$ for stiff polymers.

Next we must consider the values of r_0. This is perhaps the more important consideration in the problem. We note that the root of the determinant x, in the vicinity of the critical point x_r, is roughly of the order of t, and from our previous paragraph, also of the order of x_r. Thus, in this region, s will take values of order 1. The oscillation frequency is then always of the same scale as the screening length. Typically we will be interested in creating layers of thickness comparable, at the very least, to the radius of gyration of a chain, $R^2 \sim N$, which together with $r_0^2 \sim 1/f$, leads to the condition

$$fN \sim 1. \qquad (29)$$

For this condition to be satisfied it is required that there should be only about 1 free counterion per chain, or at least a very small number of them. The reason while this condition might still be met in practice is the possibility that many of the counterions are tightly bound to the chains in the melt, and f represents only an effective number of free counterions.

The reported findings of the Decher group [1,2], seem consistent nevertheless with this picture. While they obtain mono-layers, the thickness of the layers is relatively small, about $100 A^o$, and the observed layering occurs also under weakly charged conditions.

In the neighborhood of the critical point of the mixture the parameter s is also of order -1, which implies that

$$\chi N \sim fN \sim 1, \qquad (30)$$

which simply implies that the segregation forces should be strong enough to compensate for the loss of translational entropy of the effectively free ions. This is not a stringent requirement and many known systems can satisfy the condition.

Consider, finally, the charge density for the surface. Even when the systems is not too close to the microphase segregation point, and ϵ is not too small, the amplitude of the oscillation can be set to 1 or be over-saturated by increasing γ. If we put q charges in a surface area of size $R^2 \sim N$, we will have $\gamma \sim q/fN \sim q$. It is then clearly feasible to charge the surface with a large number of charges q in the area occupied by one chain. The approach of obtaining a large number of layers using a very strong driving force seems then easily realizable.

VI. CONCLUSIONS

We have explored the possibility of creating stable microstructures in polyelectrolytes by means of a strong external influence. While our qualitative results are consistent with experimental work, a more precise comparison with experiments cannot be done directly. We have used a number of effective parameters some elucidation is required to relate them to the bare parameters of the system. For example,it is necessary to develop a relation between the original number of charges in every chain with the *effective* number of free counterions, and also to the effective value of the χ parameter, which should also be affected as the number of condensed counterions changes. These are subjects of forthcoming research.

The only property that we have specified for the surface is its charge density, but is clear that it can be made of different materials, and in some cases the surface can already have a previous polymeric coating. The layering scenario can then occur, for example, in the neighborhood of surfaces of charged polymer brushes [10].

Another aspect of the problem that should be mention is the possibility of forcing different structures other than lamellar-like layers. When the volume fraction for one of the components is small, one could expect that, as is the case in block copolymers, the micro-segregation will create other structures, such as spherical and cylindrical domains. Of course, there would also be an interplay between the geometry of the external charged surface and the preferred geometry of the segregated system.

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